Magnetic-Field and External-Pressure Effect on Ferroelectricity in Manganites: Comparison between $GdMnO_3$ and $TbMnO_3$

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We have investigated dielectric properties in Mott insulators $GdMnO_3$ and $TbMnO_3$ under magnetic fields and external quasihydrostatic pressures. In the case of $GdMnO_3$, thermal hysteresis for dielectric constant ε and discontinuous lattice distortion were observed at ferroelectric transition temperature (T_C), and ferroelectric spontaneous polarization was suppressed by application of external pressure. These results indicate that the ferroelectric transition in $GdMnO_3$ is a first-order displacive-type one. On the other hand, the thermal hysteresis and discontinuous lattice striction were not observed at T_C in $TbMnO_3$. The peak of ε corresponding to ferroelectric transition was shifted toward higher temperatures by application of external pressure in $TbMnO_3$. The ferroelectric transition of $TbMnO_3$ was thought to be a second-order order-disorder-type one.

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The strong cross-correlation between nontrivial conjugate variables, such as electric field E vs magnetization M and magnetic field H vs resistivity ρ, has been attracted revived interest since the discovery of colossal magnetoresistance (CMR) in manganites.[1, 2] In a localized system in contrast to the itinerant one like CMR manganites, effects of the cross-correlation are observed through a magnetocapacitance or magnetodielectric response in several materials.[3, 4, 5] Since Kimura *et al*. have recently reported the magnetic control of ferroelectric polarization (so called "magnetic-field-induced electric polarization flop") in $TbMnO_3$,[6] the system in which (anti)ferromagnetic and ferroelectric properties were strongly connected has been extensively studied and some reports have been published.[7, 8]

A series of crystals of Mott insulator $R\mathrm{MnO_3}$ investigated here (R is a trivalent rare earth ion such as La^{3+}) is famous as a parent material of the CMR manganites. Above-mentioned $TbMnO_3$ is one of the series of $R\mathrm{MnO_3}$ which is not a hexagonal but a orthorhombic structure (space group $Pbnm$) with $GdFeO_3$-type distortion. $TbMnO_3$ shows an incommensurate (IC) lattice-modulation wave vector along b axis at sinusoidal antiferromagnetic transition temperature (T_N∼41K). At lower temperatures, ferroelectric phase was observed at the incommensurate-commensurate (or lock-in) magnetic transition (T_{lock}∼27K). It was thought that this ferroelectric transition originates from the sinusoidal lattice modulation induced by the magnetoelastic interaction. "Magnetic-field-induced electric polarization flop" observed in $TbMnO_3$ was thought to arise from such a strong coupling between magnetism and dielectricity. In this case, the direction of ferroelectric polarization is altered from c axis to a by magnetic fields.[6] As reported in our preceding paper[9] the ferroelectric polarization appeared in $GdMnO_3$ crystal below 13K, at which temperature Gd $4f$-spin sublattice antiferromagnetically coupled with respect to Mn $3d$ spin and the weak ferromagnetism of Mn due to the Dzyaloshinskii-Moriya interaction was suppressed. (See also the left panel of Fig.2.) This ferroelectric transition does not correspond to the IC transition (T_{IC}∼42K) or the A-type antiferromagnetic one with weak ferromagnetism (T_{N}∼20K) in Mn $3d$ spins. The direction of the ferroelectric polarization is along a axis (P_a) in orthorhombic $Pbnm$ setting, and hystereses reflecting a first-order nature of the transition were observed in thermal and magnetic-field scans. These results suggested that this ferroelectric transition was probably due to the lattice modulation connected with the magnetic transition of Gd $4f$ spins. In this work, we clarify the influence of external magnetic fields and quasihydrostatic pressures on the dielectric properties in $GdMnO_3$ and $TbMnO_3$, and discuss the difference of ferroelectric behavior between them.

Single crystalline samples were grown by the floating zone method. We performed x-ray-diffraction measurements on the obtained crystals at room temperature, and confirmed that all crystals show the orthorhombic $Pbnm$ structure without impurity phase. All specimens used in this study were cut along crystallographic principal axes into a rectangular shape with a typical dimension of $2.0 \times 1.5 \times 0.4\mathrm{mm}^3$. Measurements of temperature dependence of dielectric constant, spontaneous ferroelectric polarization, and lattice striction in magnetic fields were performed in a temperature-controllable cryostat equipped with a superconducting magnet up to 8T. Dielectric constant was measured by using LCR meter (Agilent 4284A). The spontaneous polarization was obtained by the accumulation of pyroelectric current while the sample was heated at a rate of 4K/min after cooling the sample under a poling field of 500∼300kV/m. Lattice striction was measured by using strain gauge and magnetization was measured with a SQUID magnetometer. An external quasihydrostatic pressure was produced by a clamp-type piston cylinder cell using Fluorinert as the pressure-transmitting medium.

At first, we show in Fig.1 the influence of magnetic fields on the dielectric and magnetic properties in

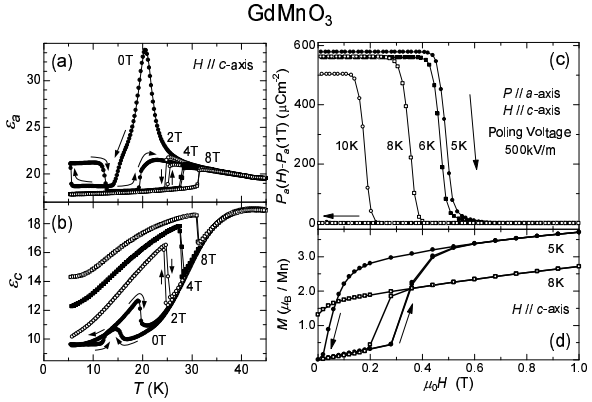

FIG. 1: Temperature dependence of dielectric constant al
a axis ε_a (a) and c axis ε_c (b) in magnetic fields (left par
In Figs. (a) and (b), the thermal hysteresis (concerning
ferroelectric phase) below 13K in 0T completely disapp
above 2T while the other hysteresis around 20K in 0T d
tically shrinks but still subsists upto 4T. Magnetic field de-
pendence of ferroelectric polarization along a axis P_a (c) and
magnetization (d) at several fixed temperatures below fer-
roelectric transition temperature T_C (right panel). In these
measurements, magnetic field is applied parallel to the c axis.
Arrows in the figure represent the scan direction.

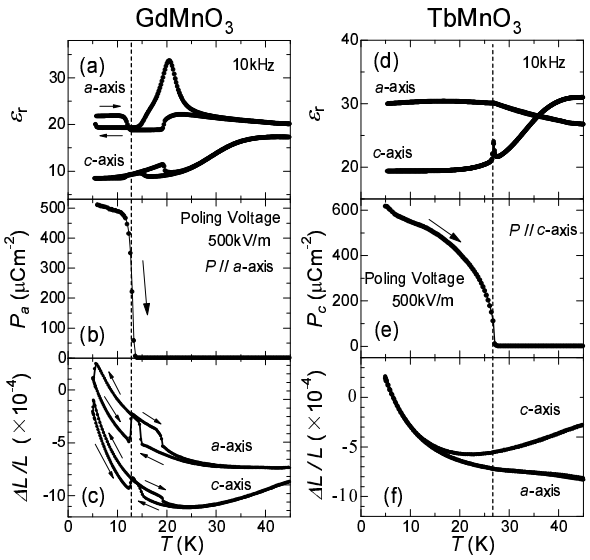

FIG. 2: Temperature dependence of dielectric constant along a and c axes (upper panels), ferroelectric spontaneous polarization (middle), and lattice striction along a and c axes (bottom) in $GdMnO_3$ (left panel: a, b, and c) and $TbMnO_3$ (right: d, e, and f). Dotted lines indicate the ferroelectric transition temperature.

$GdMnO_3$. As is already shown in our preceding paper,[9] ferroelectricity of $GdMnO_3$ in zero magnetic field exists below 13K, and is accompanied by the thermal hysteresis in dielectric constant measurement. (See also the left panel of Fig.2.) Figures 1 (a) and (b) show the temperature dependence of dielectric constant along a axis (ε_a) and c (ε_c) under magnetic fields parallel to c axis (H_c) that is perpendicular to the magnetic easy axis (b axis) in $GdMnO_3$. The thermal hysteretic region of ferroelectricity was easily suppressed by application of H_c. Figures 1 (c) and (d) show the magnetic-field dependence of ferroelectric polarization along a axis (P_a) and magnetization respectively. It turns out that P_a was collapsed by application of H_c and magnetization was increased simultaneously at the same transition field. The observed metamagnetic behavior in M-H curves is due to the spin flop of Gd $4f$ spins coupled to Mn $3d$ spins antiferromagnetically.[10] These results suggest that ferroelectricity in $GdMnO_3$ is strongly correlated to the magnetic order of Gd $4f$-spins. Furthermore, we have also performed similar measurements under magnetic fields parallel to a and b axes. The spontaneous polarization P_a was suppressed at 2.8T when a magnetic field was applied parallel to a axis (H_a) while P_a did not disappear even if magnetic field was applied up to 8T parallel to the magnetic easy axis of b (H_b). (Not shown in Fig.1.) The ferroelectric transition temperature (T_C) was shifted toward higher temperature with increase of H_b, which means that P_a was enhanced by application of H_b. These results indicate that the robustness of ferroelectric polarization P_a against magnetic fields was sensitive to the magnetic-field direction and P_a was strongly coupled with the magnetic structure, in other words, the antiferromagnetic coupling between Gd $4f$ and Mn $3d$ spins seems to be crucial to cause P_a through lattice modulation. Moreover, we have also observed the gigantic magnetocapacitance around T_N in $GdMnO_3$. The maximum value of isothermal magnetocapacitance exceeds 68% at 20K on ε_c under H_c, where the value of magnetocapacitance is defined as $\Delta\varepsilon_c(H)/\varepsilon_c(H{=}0) = [\varepsilon_c(H){-}\varepsilon_c(H{=}0)]/\varepsilon_c(H{=}0)$.

Next, we compare the behavior of ferroelectricity in $GdMnO_3$ with that of $TbMnO_3$, and discuss the difference between them. Figure 2 shows the temperature dependence of dielectric constant, ferroelectric spontaneous polarization, and lattice striction in $GdMnO_3$ (left panel) and $TbMnO_3$ (right one) in zero magnetic field. As clearly seen in the figure, ferroelectric transition in $GdMnO_3$ is accompanied by thermal hystereses and lattice distortion reflecting the nature of the first-order phase transition in contrast to the case of $TbMnO_3$. In the case of $GdMnO_3$, the magnitude of lattice striction coupled with ferroelectric transition was the order of 10^{-4} while no discontinuous jump or drop was observed at T_C in $TbMnO_3$. Moreover, the transition behavior of ferroelectric spontaneous polarization shows the first-order-like abrupt change compared with a second-order-like gradual one in the case of $TbMnO_3$. The ferroelectric transition of $GdMnO_3$ is the first-order one, on the other hand, it is thought that the ferroelectric transition of $TbMnO_3$ is the second-order one. We carried out curve fitting of spontaneous polarization P_c in $TbMnO_3$ defined as $P_c(T)/P_c(T{=}0) = [(T_C{-}T)/T_C]^{\beta}$, because of its second-order like transition. The obtained value of the critical exponent β was 0.365 which agreed well with an

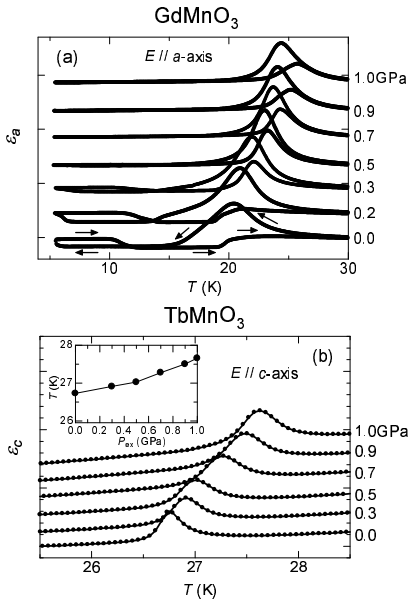

FIG. 3: Temperature dependence of dielectric constant under several fixed external quasihydrostatic pressures $P_{\rm ex}$ in $GdMnO_3$ (a) and $TbMnO_3$ (b). Note that dielectric constants in $GdMnO_3$ and $TbMnO_3$ are measured along a and c axes respectively. Vertical axes in (a) and (b) are shifted for clarity. Inset in (b) shows $P_{\rm ex}$ dependence of ferroelectric transition temperature T_C of $TbMnO_3$.

expected value for the second-order ferromagnetic transition in the three dimensional Heisenberg model.[11] This result also supports that the ferroelectric transition of $TbMnO_3$ is the second-order one, while the first-order transition in $GdMnO_3$. This conclusion is supported by other measurements including external pressure experiment discussed in the following paragraph.

Furthermore, in order to clarify the difference in mechanism of ferroelectricity between $GdMnO_3$ and $TbMnO_3$, we have performed measurements of dielectric constant under external quasihydrostatic pressure $P_{\rm ex}$. Figure 3 shows the temperature dependence of dielectric constant of $GdMnO_3$ (a) and $TbMnO_3$ (b) under several fixed pressures. In the case of $GdMnO_3$, the lower thermal hysteretic region below 13K corresponding to the ferroelectric phase was suppressed with increasing pressure and it disappears above 0.5 GPa. It seems that T_C was shifted toward lower temperatures with increasing pressure and it reached the lower temperatures that we can not obtain. The tendency that T_C shifts toward lower temperatures with increasing pressure is a typical characteristic of a displacive-type ferroelectric transition under external pressure.[12] The obtained tendency, therefore, implies that the ferroelectric transition of $GdMnO_3$ is the displacive-type one. In the perovskite structure, many displacive-type-ferroelectric materials such as $BaTiO_3$, $PbTiO_3$, $LiTaO_3$, and so on have actually been reported. Then it seems reasonable to conclude that the ferroelectric transition of $GdMnO_3$ is the first-order displacive-type one. On the other hand, in the case of $TbMnO_3$, the dielectric constant peak corresponding to the ferroelectric transition is shifted toward higher temperatures with increasing pressure. This behavior is a typical characteristic of a order-disorder-type ferroelectric transition under external pressures.[12] This result also supports that the ferroelectric transition of $TbMnO_3$ is the second-order order-disorder-type one.

Although $GdMnO_3$ and $TbMnO_3$ are nearly same crystal structure with slight different orthorhombic distortion,[5] there may exist similar or distinct behavior of ferroelectricity between them. In $TbMnO_3$, the ferroelectric polarization along a axis ($P_a^{\rm Tb}(H{\neq}0)$) is flopped from c axis ($P_c^{\rm Tb}(H{=}0)$ induced by magnetic fields. $P_a^{\rm Tb}(H{\neq}0)$ accompanied by hysteresis was observed, only when the magnetic field was applied parallel to b axis. The spontaneous polarization of $GdMnO_3$ along a axis in zero field ($P_a^{\rm Gd}(H{=}0)$) was enhanced only when the magnetic field was applied parallel to the same b axis, and it was accompanied by hysteresis at T_C. As discussed in previous paragraph, transition character between $GdMnO_3$ and $TbMnO_3$ in zero magnetic field is quite different from each other. However, as mentioned above, there are many common features between $P_a^{\rm Tb}(H{\neq}0)$ and $P_a^{\rm Gd}(H{=}0)$. These facts may imply that $P_a^{\rm Tb}(H{\neq}0)$ has a similar origin of $P_a^{\rm Gd}(H{=}0)$, which cannot be revealed in detail at present, although $P_c^{\rm Tb}(H{=}0)$ seems to have quite different origin from $P_a^{\rm Gd}(H{=}0)$.

In summary, we have studied the influence of magnetic field and quasihydrostatic pressure upon the dielectric properties in single crystals of $GdMnO_3$ and $TbMnO_3$. Contrast to the case of $TbMnO_3$, "magnetic-field-induced electric polarization flop" was not observed in $GdMnO_3$. The robustness of polarization in $GdMnO_3$ $P_a^{\rm Gd}$ against magnetic fields has the large anisotropy respect to the field direction. This indicates that $P_a^{\rm Gd}$ was strongly reflected by the large anisotropy of magnetic structure, i.e., antiferromagnetic coupling between Gd $4f$ and Mn $3d$ spins. The collapse of $P_a^{\rm Gd}$ seems to arise from change of lattice modulation coupled magnetoelastically with the metamagnetic transition of Gd $4f$ spins. By comparing the experimental results in the cases of $GdMnO_3$ and $TbMnO_3$, the transition character of $P_a^{\rm Gd}(H{=}0)$ seems to be similar to $P_a^{\rm Tb}(H{\neq}0)$ which is flopped from $P_c^{\rm Tb}(H{=}0)$ by application of magnetic field parallel to the b axis H_b. On the other hand, the origin of $P_a^{\rm Gd}(H{=}0)$ and $P_c^{\rm Tb}(H{=}0)$ is likely to be different: The former should be classified as the first-order displacive-type transition and the latter as the second-order order-disorder-type one. The observed coupling between ferroelectric and magnetic properties is expected to bring a possible multifunctional device with cross-correlation such as magnetically-recorded ferroelectric memory in the future.

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